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Evaluation and analysis of the performance of dehydration units for CO_2 capture

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Abstract

The dehydration step is a relatively small part within the full carbon dioxide capture and storage (CCS) chain, yet this unit plays an important role in maintaining the integrity of the system. In the past, this step usually appeared as a black box process, with little information available on its detailed design. However, the conventional drying technologies face a number of challenges that need consideration before full-scale deployment.
IEAGHG commissioned AMEC to assess the characteristics and performance of the various drying processes and their integration into the CCS system. This work evaluates dehydration processes that are able to reach water contents ranging from 600 ppmv down to < 10 ppmv, with a focus on TEG (triethylene glycol) and molecular sieve systems. It considers a range of flow rates, constraints on the dehydration pressure and the range of other substances in the CO_2 gas.

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Keywords: CO_2 capture, CO_2 dehydration, molecular sieve, TEG (triethylene glycol), process design , costs, integration

1. Introduction

Within the full carbon dioxide capture and storage (CCS) chain, the dehydration step is a relatively small part, yet this unit plays an important role in maintaining the integrity of the whole system. In the past, this step usually appeared as a black box process, with little information available on its detailed design. However, the conventional drying technologies face a number of challenges that need consideration before full-scale deployment of CCS.

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The CO_2 streams produced by the various combustion and capture processes are of different quality, containing different types and concentrations of inerts and impurities. These differences can significantly affect the design and operation of a CO_2 dehydration unit. Furthermore, the dehydration unit is a critical process that provides moisture integrity for the downstream transportation and injection systems. The list below explains the differences between the various CO_2 capture processes, which are relevant to dehydration:

- Post combustion capture usually delivers a water-saturated CO_2 rich gas from the stripper condenser at pressures just above atmospheric.
- Pre-combustion capture provides multi-stream CO_2 gases from the acid gas removal (AGR) unit at low pressure and medium pressure conditions.
    - The Rectisol [1] process delivers dry CO_2 gas at < 1 ppmv moisture containing small levels of methanol [2]. The gas does not require further drying and the methanol content will usually not condense out in the subsequent compression and/or cooling process. Hence, this work will not consider the Rectisol process further.
    - The Selexol [3] solution contains water, so the process supplies a water-saturated CO_2 gas. Selexol has a low vapour pressure so there is minimal contamination of the dry CO_2 stream. Water levels of around 500–1000 ppmv are achievable, but only at pressures in excess of 10 barg with a CO_2 purity of less than 98% [4].
- CO_2 rich gas from oxyfuel combustion will have a wide variation of composition and pressure dependent on the technology selected for the CO_2 processing unit (CPU). The gas entering the dehydration unit is water-saturated and contains inerts and other trace amounts of acidic components – mostly the residual NO_x from the upstream removal process.

It is necessary to dehydrate the CO_2 stream from the majority of CO_2 capture processes prior to transportation in carbon steel pipelines. Low moisture content is critical in prevention or minimisation of both corrosion in carbon steel pipe work and hydrate (i.e. solid crystalline compounds) formation. The selected process must therefore be robust and reliable while minimising the introduction of any additional impurities to the CO_2.

In general, the following different types of dehydration techniques exist for drying of gases and are suitable for CO_2 streams:

- Cooling (e.g. compressor inter-stage cooling)
- Joule Thomson cooling (adiabatic cooling via gas expansion)
- Refrigeration (gas cooling with a refrigerant
- Turbo expansion (isentropic cooling with gas expansion)
- Supersonic separation (gas expansion to supersonic velocity in a Laval nozzle and subsequent separation of the formed liquid droplets in a cyclone)
- Solid desiccants
    - Silica gel (SiO_2)
    - Activated alumina (Al_2O_3)
    - Molecular sieves (synthetic zeolite aluminosilicates, especially types 3A and 4A are suitable for CO_2 dehydration)
- Liquid desiccants
    - Methanol (e.g. Ifpexol [5])
    - Glycerol [6, 7, 8]
    - Triethylene glycol (TEG) [9] (further developments of the standard TEG process are the Drigas, DRIZO and Coldfinger processes [5, 10])
    - Other glycols (such as ethylene glycol (EG), diethylene glycol (DEG) and tetraethylene glycol (TREG)) [9]
- Membranes (not used to date on either CO_2 separation or CO_2 dehydration duties [11] but research and development in this area is ongoing [12, 13, 14])

Some of the techniques do not achieve low moisture levels. However, they are straightforward, low cost processes, often required in a process anyway (such as compressor inter-stage cooling and knockout), so they are important in offloading the main dehydration unit (e.g. TEG or molecular sieve system). This can lead to smaller, less costly dehydration systems. At the moment, vendors participating in this study see molecular sieve and TEG systems as the ones that are most likely for CCS applications.

Fig. 1 shows the outline of a molecular sieve dehydration process that uses pressurized CO_2 for regeneration. It is a two-bed system, where the spent regeneration gas is returned to the inlet of the adsorption bed. Fig. 2 provides a schematic layout of a simple TEG dehydration process. Both figures present the basis for the calculation of the heat and mass balances of the dehydration processes later in this paper. More detailed information about the various design options of molecular sieve and TEG processes is available in the study report [15].

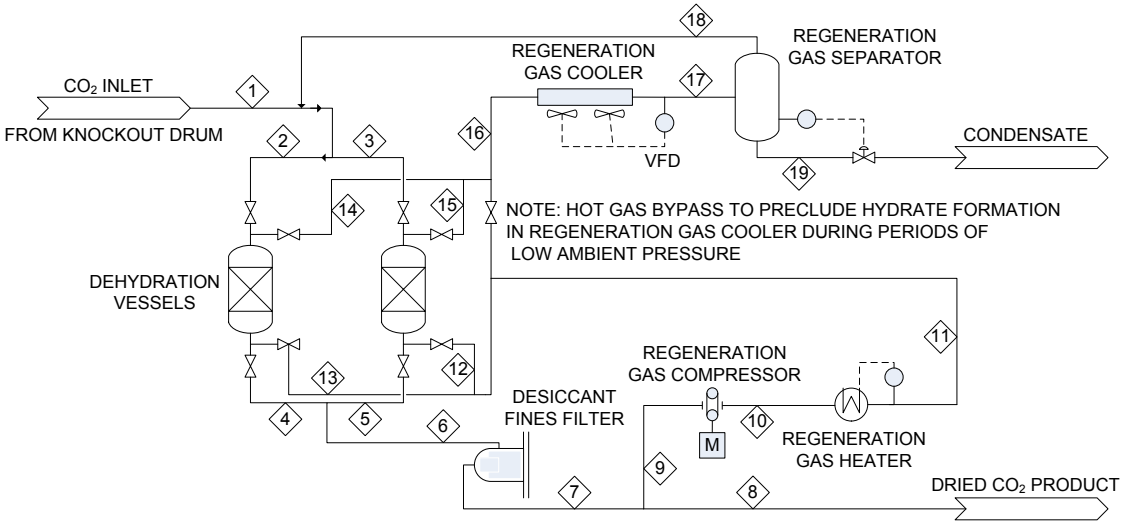

Fig. 1. Schematic of a molecular sieve dehydration unit.

It is important to quantify and control impurities and inerts, as they can lead to significant changes in the physical properties of the CO_2 stream. For example, presence of SO_2 can reduce the dense phase density by around 14%, whereas systems containing H_2 can exhibit two-phase regions if the pressure exceeds 120 barg [16]. CH_4 and N_2 can significantly reduce the saturated water content of pure CO_2. A H_2S concentration of 200 ppm can result in an increase of water solubility, which is not problematic, but a CH_4 concentration of 5% can decrease the water solubility significantly by 30% [17].

In addition, impurities can affect the desiccant and result in higher rates of corrosion. In presence of water, CO_2 forms carbonic acid and acidic impurities, such as H_2S, NO_x and SO_x, can also lead to or accelerate corrosion [18, 19]. It is possible to minimise corrosion from CO_2 and most acidic impurities by preventing water dewing, however, this does not work for H_2S induced corrosion.

Another issue is that in presence of water CO_2 can form hydrates in both vapour and liquid phase [20]. Hydrate formation can also occur with H_2S, and other solids, such as ammonium carbamate, carbonate and bicarbonate may form when CO_2 meets and reacts with NH_3. These solids can potentially cause severe blockages in the compression, dehydration, transportation and injection systems of the CCS chain, so might require the use of chemical inhibitors or other prevention strategies, like changing the operating conditions. One reference suggests “full” dehydration to 50 ppmv or a water content of no more than 60% of the dew point [21]. Other references, like the report of the DYNAMIS project [16], argue that this requirement is too stringent. The most likely point of hydrate formation is upstream the dehydration unit in the suction and discharge coolers of the compression train.

Furthermore, water ice or liquid CO_2 can form when cooling wet CO_2 gas below certain limits of pressure and temperature. A crossover region of hydrate, water ice and liquid CO_2 formation exists for selected temperature and pressure conditions, resulting in an allowable operating window [22].

So it is important to take the above mentioned issues into account when selecting target product moisture and operating conditions of the dehydration unit. There is also a wide range in dry CO_2 moisture specifications used for pipelines in the literature. Likewise, these specifications will influence the selection of the appropriate dehydration technique.

However, as the effect of impurities and inerts are not yet fully understood, they need further research and quantification. The adequate modelling of the physical properties of CO_2 containing inerts and impurities would also require new or modified equations of state.

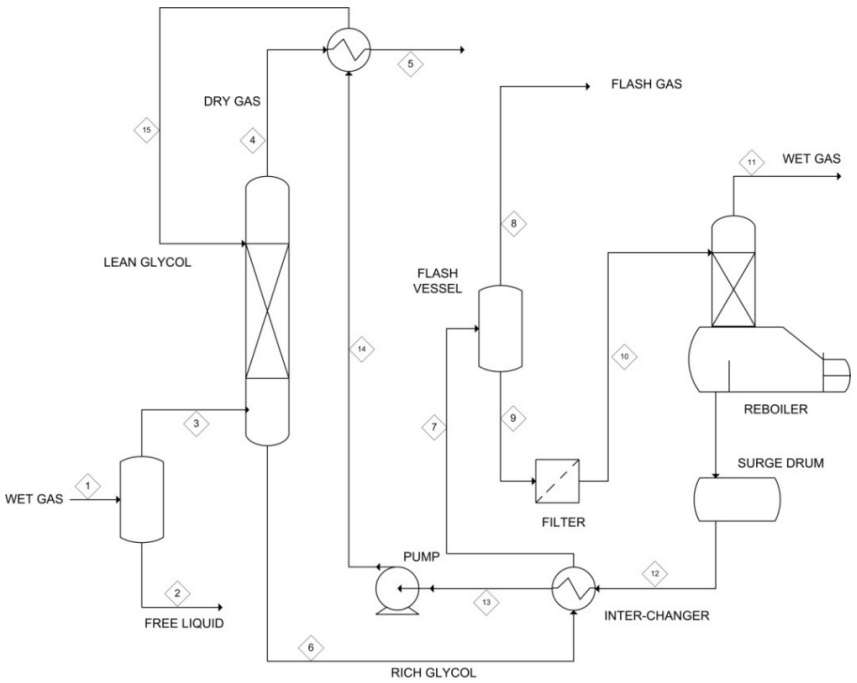

Fig. 2. Schematic of a TEG dehydration unit.

2. Approach

The scope of work for this assessment comprises four main elements:

- Evaluation and characterization of processes for the dehydration of captured CO_2
- Evaluation of methods for monitoring and management of water dryness
- Preparation of guidance on process selection to match the various requirements for water dryness of CO_2
- Analysis of future drying technology developments

AMEC used information available from the different capture processes to produce a set of dehydration feed gas compositions. Base case data represent minimum or normal impurity levels. Three additional cases consider higher levels of impurities and inerts. Tab. 1 provides the CO_2 stream composition and conditions for the different CO_2 capture technologies and the step-off cases.

Tab. 1. Summary of dehydration unit inlet conditions and composition.

		Post-combustion capture	Pre-combustion capture	Oxy-fuel combustion		High inerts	High impurities	
			Selexol	High pressure	Low pressure		High O_2	High NO_x, SO_x, H_2S
Components	**Units**							
CO_2	Mol% dry	99.94	98.38	75.86	75.86	95.94	99.94	99.94
H_2O	Mol%	sat	sat	sat	sat	sat	sat	sat
N_2	Mol% dry	0.05	0.0072	15.22	15.22	4	0.05	0.05
Ar	Mol% dry	0	0.065	2.45	2.45	0	0	0
H_2	Mol% dry	0	1.26			0	0	0
CH_4	Mol% dry	0	0.0024	0	0	0	0	0
O_2	-	30 ppmv	0	6.24 %	6.24 %	30 ppmv	300 ppmv	30 ppmv
CO	-	10 ppmv	0.279%	50 ppmv	50 ppmv	10 ppmv	10 ppmv	10 ppmv
NO_x	ppmv	30	0	60	82	30	30	100
SO_2	ppmv	15	0	170	0	15	15	100
H_2S	ppmv	1	1	0	0	1	1	100
COS	ppmv	0	16	0	0	0	0	0
HCl	ppmv	1	0	0	0	1	1	1
Amines	ppmv	1	0			1	1	20
NH_3	ppmv	5	0	0	0	5	5	5
Aldehydes	ppmv	20	0	0	0	20	20	20
Conditions								
Temperature	ºC	30	30	30	30	30	30	30
Pressure	Bara	30	30	30	5	30	30	30

This work investigates three different moisture levels: 550 ppmv (typically used in pipeline systems that experience relatively high ambient temperatures), 50 ppmv and < 10 ppmv (typically required where downstream processing involves low temperature or cryogenic conditions).

Two different CO_2 flow rates were considered : 265 te/hr (typical amount of CO_2 captured from a 1 GW_e gas-fired power plant with at least 85% capture rate), and 600 te/hr (typical mass flow for a 1 GW_e coal-fired power plant with at least 85% capture rate).

Dehydration package vendors provided economic and technical data, including the maximum rate achievable for a single dehydration train. Dehydration media vendors assisted with estimates of the number of beds and bed size. They were also able to help with information on the effects of impurities, in particular on molecular sieve adsorbents, and the role of side reactions.

Data presented in the cost section is a combination of data received from different vendors, data from previous AMEC projects and AMEC modelling and cost estimation. Cost data presented in this paper is mainly in the form of

cost indicators, due to reasons of vendor confidentiality. The basic criteria for the techno-economic comparison were taken from previous IEAGHG work [23, 24].

3. Results and discussion

Information from both package vendors and media vendors centered around two basic process mediums: TEG and molecular sieves. Because of this, the following discussion focusses on these two media. As data was lacking, it was not possible to adress all cases presented in Tab. 1, so the focus is on a generic post-combustion capture process with step-off cases for high impurities and high inerts.

3.1 Evaluation of technical plant performance

For post-combustion and pre-combustion capture a variety of different dehydration pressures is possible. This depends on the available supply pressure and compressor interstage conditions. Oxyfuel cases span a range of pressures from 5-30 bara, dependent on the supply pressure and downstream processing requirements.

Low-pressure operation will require larger diameter beds and larger bed volumes to cater for the higher volume of gas and the increase in moisture content. Depending on the operating conditions, expected lifetime of molecular sieves lies between 2-4 years and TEG lifetime varies between 3-10 years, typical for both is an average of 3 years.

Molecular sieve systems can easily achieve target moisture contents of 1 ppmv, while standard TEG processes can get down to around 150 ppmv. For lower moisture targets, advanced TEG processes (e.g. Drigas, DRIZO, Coldfinger) are necessary. Increasing the TEG concentration by various methods can achieve drying performances of down to 30 ppmv.

The maximum train size appears to vary considerably. For molecular sieve cases with feed gas at 30 bara and 30°C the range (from different vendors) varied between 300-600 te/hr and between 100-120 te/hr for 5 bara and 30°C. The limitations depend on several factors including the maximum vessel diameter, the capital cost of the vessel, the maximum number of beds of a certain size in parallel, the adsorption time of each bed and the regeneration rate. It is desirable to keep the bed size small to avoid the requirement for large volumes of desiccant and associated vessels. At a certain point, it is more practical to split the feed across an additional number of trains.

Preliminary estimates show that a TEG regeneration unit can handle the moisture of up to 3,500 te/hr of CO_2 rich gas, although this quantity would perhaps require multiple contactors due to the large gas volume that needs processing.

A dehydration unit capacity of 265 te/hr would require 48-102 te of molecular sieve adsorbent and around 30 t of TEG absorbent. Future expansion of capacity is possible for both molecular sieve and TEG systems if the original design allows for additional beds/contactors. The footprints of the dehydration packages vary greatly, especially for molecular sieve systems with different regeneration methods, e.g. pressurized regeneration with CO_2 can have approximately 2-3 times the dimensions of a low pressure regeneration layout [15].

3.2 Effects of impurities and inerts

Tab. 2 contains a summary of the currently known effects of impurities and inerts, including their maximum tolerable concentrations (if known), on molecular sieve and TEG systems.

In the case of solid desiccant systems, the following approaches are generally helpful for dealing with impurities:

- Additional amounts of desiccant can cater for the effects of impurities, e.g. co-adsorption
- Use of an acid-resistant desiccant (e.g. type 3A or 4A), which can better withstand the impurities
- Applying sacrificial or regenerable guard beds that can tolerate acidic impurities (e.g. activated alumina or silica gel)

In the case of liquid desiccants, impurities can form solids, cause foaming or react with the desiccant to build corrosive products. The below mentioned measurements can assist with addressing these issues:

- In-line filtration
- High-efficiency column internals
- Anti-foam
- Degradation/corrosion inhibitors

Sometimes the levels of impurities are not acceptable, because of either their damaging effects or the increase in necessary dehydration media volume. In this case, removal of the impurities in a separate upstream process is an option. It will be essential to discuss specific impurities and their normal as well as maximum concentrations with the vendor during the design stage.

Section 3.4 of this paper contains an assessment of the effect of impurities, in particular O_2, NO_x, SO_x and H_2S, and inerts, represented by N_2, on capital and operating costs.

Tab. 2. Effects of impurities on TEG and molecular sieve dehydration systems.

Impurity	**Effect on TEG system**	**Max. tolerable conditions**	**Effect on mol. sieve system**	**Max. tolerable conditions**
H_2O	Formation of liquid droplets and mist can weaken absorption capacity	?	Formation of liquid droplets and mist can exhaust the sieve or react with the binder causing breakdown of the structure	?
Inerts (N_2, Ar, H_2, CH_4)	No effect	No limit	No effect	No limit
O_2	Oxidative degradation of TEG	?	If hydrocarbon present: coke formation, pore blockage; if sulfur present: blockages	15-50 ppm (one vendor stated no limitation)
H_2S	?	3000 ppm	Acid degradation of sieve, COS can form; if O_2 present: formation of SO_2 and free sulfur, corrosion	0-1000 ppmv (nil if O_2 present)
NO_x, SO_x	?	?	Attack sieve structure, reducing lifetime, acids can form during regeneration	?
HCl, other acids	Lower pH causes corrosion	200-300 ppm chlorides, pH 6-9	Dealumination of zeolite framework, causing dust formation	0-1 ppmv (higher if acid-resistant sieves and/or sacrificial guard beds are used)
CO	?	?	No effect	No limit
COS	?	?	Type 4A sieves can catalyze COS formation, which can break down into H_2S and CO_2, increasing corrosion	?
Amines	Foaming	?	Permanent damage to sieve, leading to dust formation, coking due to NH_3 and NH_4^+ formation	?
Aldehydes	Change in pH, corrosion, foaming	?	Coking, aldol condensation, polymerization (formed products are highly toxic)	200 ppmv
Methanol	Column flooding	?	Co-adsoprtion, premature breakthrough, formation of H_2	240°C

			and CO	
NH_3	?	?	Co-adsorption, if H_2O(l) present: ion exchange weakens sieve structure	? (5-10 ppmv added capacity necessary)
Glycols	?	?	Adsorption by sieve binder can cause premature aging, polymerization, coking, cementing can result in channeling of the bed	?
NaCl	Corrosion	?	Pore blockage, structural damage to binder and sieve, dust formation, agglomeration	?

3.3 Heat and mass balances for molecular sieve and TEG system

Tab. 3 contains the heat and mass balance for a molecular sieve package that uses pressurised CO_2 for regeneration according to Fig. 1. The case is a snapshot of a two bed system with the spent bed part way through regeneration, i.e. the bed is partially heated. Spent regeneration gas is returned to the inlet of the adsorption bed.

Tab. 4 provides the heat and mass balance for a generic TEG dehydration system according to the outline PFD in Fig. 2. In modelling the process it is apparent that the impurities in the system and the water-CO_2-glycol interactions are not well defined and require further work. The information provided by this model is simple, it does not consider the potential to recover flash gas or CO_2 in the wet gas from the regeneration still. Further more detailed analysis should be sought from the appropriate vendor. The energy demand of the regeneration column reboiler is provided for information, energy requirements of pumps in the system are dependent on configuration and are therefore not quoted.

Tab. 3. Heat and mass balance for molecular sieve dehydration unit (post-combustion case at 265 te/hr).

Stream	1	2	3	4	5	6	7	8	9	10
Temperature (°C)	30	30	30	29.2	29.2	29.2	28.9	28.9	28.9	34.5
Pressure (Bara)	30	30	30	29.3	29.3	29.3	29	29	29	30.6
TOTAL FLOW										
Mass Flow (kg/hr)	265,000	302,940	0	302,655	0	302,655	302,655	264,822	37,832	37,832
Molar Flow (kg-mol/hr)	6,031	6,894		6,878	0	6,878	6,878	6,018	860	860
GASEOUS PHASE										
Mass Flow (kg/hr)	265,000	302,940	0	302,655	0	302,655	302,655	264,822	37,832	37,832
Molar Flow (kg-mol/hr)	6,031	6,894		6,878	0	6,878	6,878	6,018	860	860
Molecular Weight	43.9	43.9	43.9	44.0	44.0	44	44	44.0	44.0	44.0
Composition (mol %)										
CO_2	99.72	99.72	99.72	99.95	99.95	99.95	99.95	99.95	99.95	99.95
H_2O	0.23	0.23	0.23	0	0	0	0	0	0	0
N_2	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
LIQUID PHASE										
Mass Flow (kg/hr)										

Stream	11	12	13	14	15	16	17	18	19
Temperature (°C)	230	230	230	120	120	120	30	30	30
Pressure (Bara)	30.4	30.4	30.4	30.4	30.4	30.4	30.2	30	30
TOTAL FLOW									
Mass Flow (kg/hr)	37,832	37,832	0	0	38,318	38,318	38,318	37,854	464
Molar Flow (kg-mol/hr)	860	860	0	0	887	887	887	861	26
GASEOUS PHASE									
Mass Flow (kg/hr)	37,832	37,832	0	0	38,318	38,318	37,854	37,854	0
Molar Flow (kg-mol/hr)	860	860	0	0	887	887	862	862	0
Molecular Weight	44.0	44.0	44.0	43.2	43.2	43.2	43.9	43.9	
Composition (mol %)									
CO_2	99.95	99.95	99.95	96.91	96.91	96.91	99.72	99.72	
H_2O	0	0	0	3.04	3.04	3.04	0.23	0.23	
N_2	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	
LIQUID PHASE									
Mass Flow (kg/hr)							463.7		463.7

Tab. 4. Heat and mass balance for TEG dehydration unit (post-combustion case at 265 te/hr).

Stream	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Temperature (°C)	30	30	30	30	31	31	110	98	98	98	102	204	121	120	60
Pressure (Bara)	30.00	30.00	30.00	28.00	27.66	30.00	29.31	1.10	1.10	1.10	1.01	1.03	1.03	28.00	28.00
TOTAL FLOW															
Mass Flow (te/hr)	265	0	265	264	264	3.5	3.5	0.3	3.2	3.2	0.2	2.99	2.99	2.99	2.99
Molar Flow (kg-mol/hr)	6,021	0	6,021	6,003	6,003	40.3	40.3	9	31.5	31.5	11.2	21.4	21.4	21.4	21.4
GASEOUS PHASE															
Vapour Fraction	1	0	1	1	1	0	0	1	0	0	1	0	0	0	0
Composition (mol%)															
CO2	99.72	1.20	99.72	99.93	99.93	15.11	15.11	68.22	0.30	0.30	10.95	0.00	0.00	0.00	0.00
H20	0.22	98.80	0.22	0.01	0.01	35.70	35.70	31.60	36.84	36.84	88.96	7.51	7.51	7.49	7.46
N2	0.05	0.00	0.05	0.05	0.05	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TEG	0.00	0.00	0.00	0.00	0.00	49.14	49.14	0.06	62.82	62.82	0.04	92.47	92.47	92.49	92.52
Key Energy															
Regeneration Reboiler	368	kW													

3.4 Evaluation of economic plant performance

Data presented in this section is a combination of data received from different vendors, data from previous AMEC projects and AMEC modelling and cost estimation. The figures show the cost numbers as uninstalled equipment costs in the form of cost indicators, due to reasons of vendor confidentiality. A cost indicator of "x" represents x-times the cost of the baseline cost of "1". In general, the capital costs of dehydration equipment are a minor part of the overall costs for a CCS plant.

3.4.1 CAPEX of molecular sieve and TEG systems

Fig. 3 plots the cost indicator for molecular sieve systems against CO_2 flow rate and shows the maximum and minimum cost lines. There is a wide spread in molecular sieve capital cost data from different vendors for a fixed operating pressure. The differences are due to several factors:

- The regeneration techniques proposed by different vendors. Atmospheric pressure regeneration with air will be less costly. The amount of equipment required is significantly lower than for a high-pressure regeneration using CO_2. The volume of CO_2 gas passing through the online bed is also lower, so smaller bed size results.
- Use of the CO_2 compression facility to provide the driving force for the regeneration gas results in less equipment for the dehydration package but larger compression and cooling equipment and higher compression costs.
- The materials of construction proposed.
- The number and size of the individual adsorption beds proposed.
- The number of parallel dehydration trains proposed.

Operating pressure has an effect on the equipment capital costs of molecular sieve systems. Limited available data indicates that equipment capital cost passes through a minimum at 25–30 bara [25]. The actual location of the minimum is application specific and depends on:

- The same reasons that cause differences in capital cost (see above).
- The equipment design pressure (whether it is set to be 10% above the maximum operating pressure or designed for compressor settle out pressure on compressor trip).
- The type of regeneration and the extent of regeneration equipment.

There is no difference between the capital costs of the molecular sieve equipment for target moistures of 550 ppmv, 50 ppmv and < 10 ppmv. Media suppliers and package vendors all advised that it is normal to design for the removal of water from the gas stream to achieve < 1 ppmv, irrespective of the target moisture required. However, at lower target moisture, the cycle time of each bed becomes shorter.

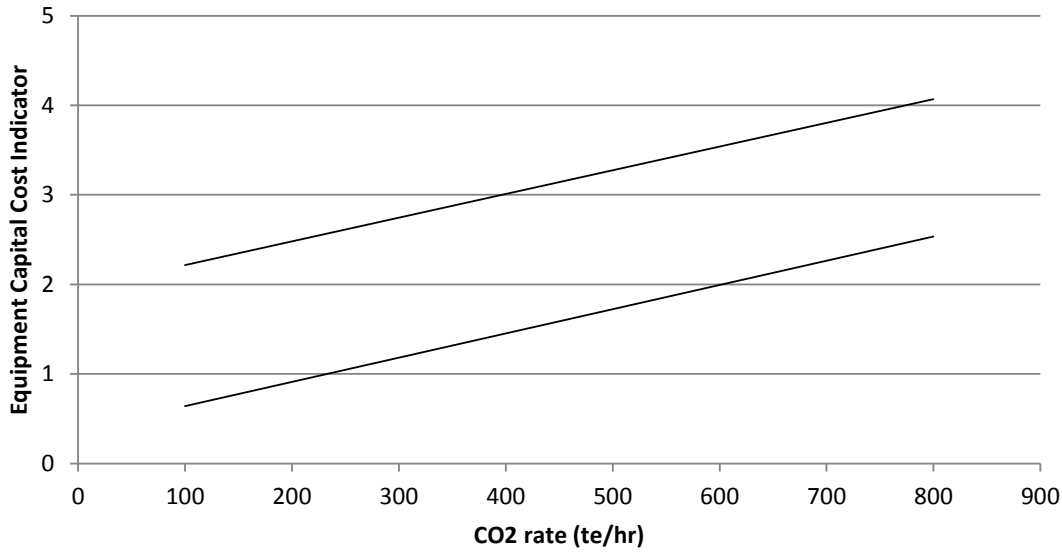

Fig. 3. CAPEX indicator for molecular sieve.

Data on liquid desiccants, i.e. TEG, is lacking. The available data is for water-saturated raw gas at 30 bara and 30°C. The raw gas stream is relatively pure containing > 99% CO_2 with low levels of impurities. Target product moisture is 50 ppmv, and the TEG process includes the use of stripping gas to increase the TEG concentration. Fig. 4 shows the equipment capital cost indicator as a function of CO_2 flow rate for this system. Vendors consider the line to represent a maximum cost line.

Higher levels of target product moisture (i.e. greater than 150 ppmv) will require only basic equipment, so the stripper will not be necessary. The cost for such a system will therefore be lower.

In case of high impurities:

- Increased oxygen levels of 300 ppmv have no effect on the molecular sieve equipment cost. However, oxygen can degrade TEG. It was not possible to quantify the effect on TEG equipment capital cost because the exact acceptable limits are unknown.
- The case with 100 ppmv NO_x, 100 ppmv SO_2 and 100 ppmv H_2S results in:
    - The use of an acid-resistant molecular sieve with an increase in media volume of ~ 5% and an increase in media cost of ~ 15%. Molecular sieve equipment capital cost will be ~ 7% higher.
    - Again, it was not possible to quantify the effects on TEG equipment capital cost.

A clear recommendation is to discuss impurity issues with the vendor at an early stage, as an upstream removal system might be advantageous or essential.

In case of high inerts content the cost of the equipment per tonne of CO_2 will be higher than for a low inerts gas. The reasons for this are mainly:

- The increased volume of raw gas per te of CO_2 requires a larger diameter TEG contactor or larger diameter solid desiccant bed.
- The gas carries a higher amount of water that needs removal. The circulation rate of TEG and the equipment in the TEG circulation loop will therefore increase. Similar, molecular sieve systems will require larger media volumes. This results in a higher capital cost for both systems.

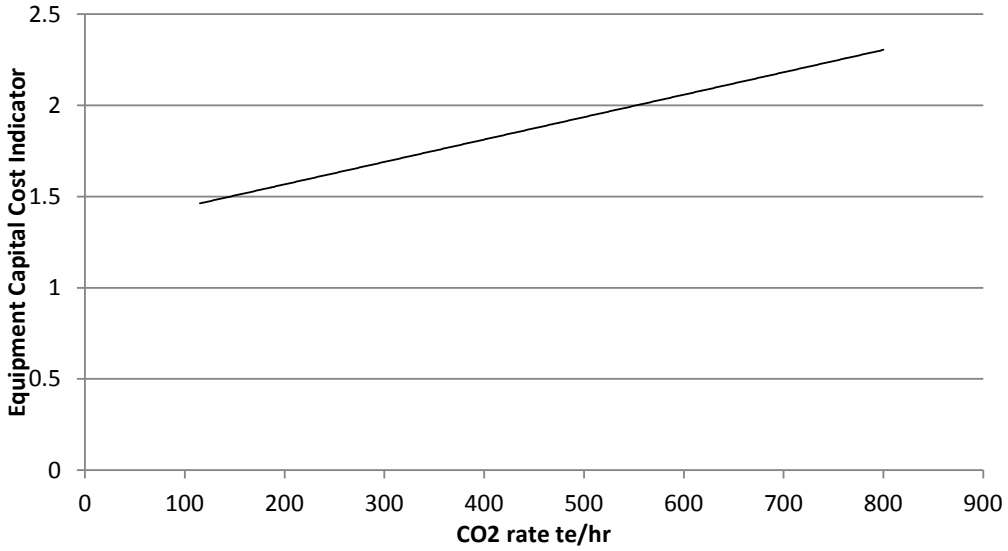

Fig. 4. CAPEX indicator for TEG.

3.4.2 OPEX of molecular sieve and TEG systems

Fig. 5 presents the results of the operating cost estimation for the following cases, both assuming a desiccant lifetime of 3 years:

- Molecular sieve at 265 te/hr – Options from two different vendors, one using low pressure regeneration with atmospheric air (minimum CAPEX case) and another using CO_2 at pressure for regeneration (maximum CAPEX case).
- TEG at 265 te/hr – Only a single vendor (who also provided the molecular sieve maximum CAPEX case data) has provided information.

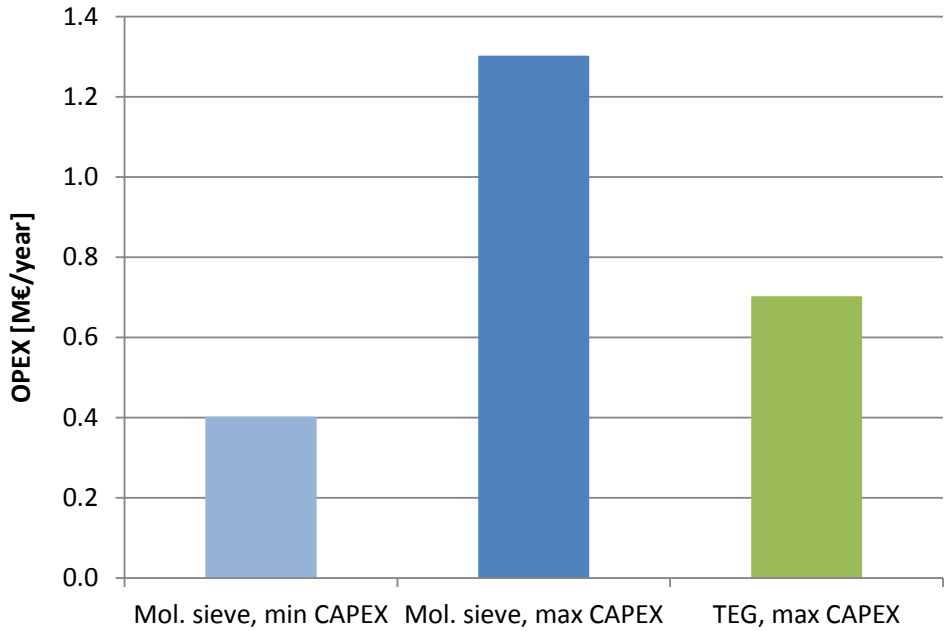

Fig. 5. OPEX estimates for different dehydration systems.

Comparing data from the same vendor indicates that the annual operating cost of the TEG system is significantly lower than that for the molecular sieve package. However, the more basic molecular sieve package, from a different vendor, but for the same raw gas conditions, indicates that the annual operating costs for molecular sieve systems can also be significantly lower than those for a TEG system. The estimated minimum operating costs for molecular sieve packages as a function of CO_2 flow rate follow a linear trend, comparable to the CAPEX indicators in Fig. 3 and 4. They span a range from 0.27 M€/yr for a capacity of 265 te/hr and 0.72 M€/yr for a unit size of 800 te/hr [26].

The limited information available from vendors suggests that operating pressure has an effect on operating costs, and that the regeneration power consumption will pass through a minimum. The actual minimum pressure will vary for individual applications.

The vendor data also indicates that the effect of impurities on molecular sieve operating cost is insignificant. The increased bed volume mainly results in higher capital cost, which impacts onto maintenance costs, taxes and insurance. Desiccant cost increases as well, but regeneration power consumption will be lower.

3.5 Techno-economic evaluation of moisture monitoring equipment

Monitoring of the drying performance ensures that water breakthrough does not occur. It is important to use a continuous monitoring system, because manual sampling and analysis will not be sufficient. The presence of CO_2 itself and the potential contaminants limit the number of available analysis techniques. Participating vendors proposed a range of different physico-chemical measuring principles:

- Laser absorption spectroscopy: tuneable diode (TDLAS) and cavity ring down (CRDS)
- Phosphorous pentoxide (P_2O_5) coated cell
- Quartz crystal cell
- Silicon sensor

Fig. 6 provides relative cost data for moisture monitoring equipment. The cost indicator values exclude the sampling system and analyser housing/building, as these requirements are very project specific. The figure shows that P_2O_5 cells are the least expensive moisture measuring technique, although the cost can vary significantly between differrent vendors. Quartz crystal sensors and CRDS are the most expensive techniques (i.e. when omitting the dual silicon sensor set-up).

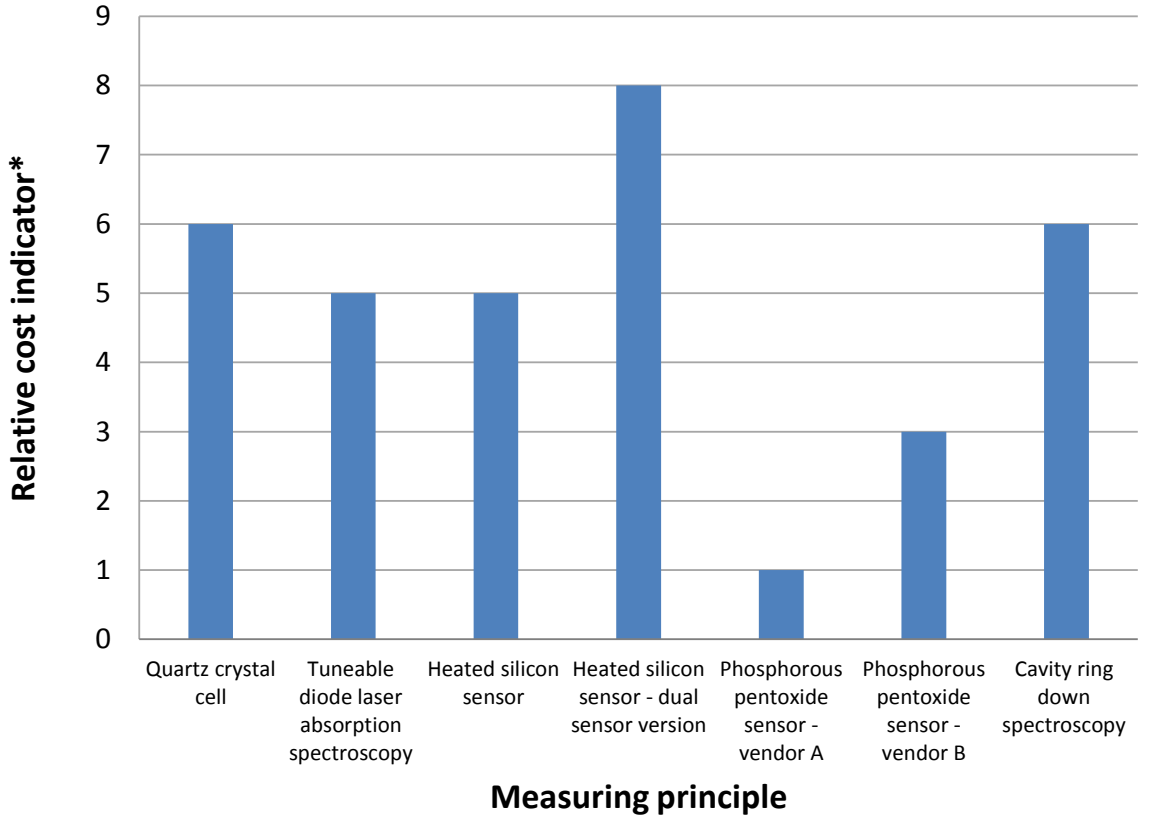

Fig. 6. Relative cost indicators for different moisture monitoring techniques. (*where, e.g., 5 indicates that the item price is 5 times as costly as the baseline price of 1)

All techniques can measure down to very low ppm levels; the P_2O_5 sensor of vendor B and the CRDS are capable of achieving ppb levels. As with the desiccants, impurities play an important role, so it is necessary to discuss the issue with the vendors to select the most appropriate technique and device. The quartz sensor can react sensitive towards NH_3 and Hg, whereas polar molecules and hydrocarbons above C_6 can interfere with the silicon sensor. Vendor A of the P_2O_5 cell stated that MeOH and Hg can affect the moisture reading and that amine vapour is a particular issue, as exposure to 10 ppm over one week can deactivate the surface of the P_2O_5 cell, requiring re-coating of the sensor.

The sampling system can significantly influence the overall performance and recovery time from upset conditions. Sampling usually involves pressure let-down and the related Joule Thomson chilling can result in condensation of any of the components present. Because this can affect both the analyser and the analysis result, vendors generally recommend sample heating systems. To avoid damage or prolonged erroneous readings under upset conditions, the design of the sensor needs to consider these conditions.

Maintenance frequency depends on the gas quality. Particulates are a particular issue for some types of device, such as the P_2O_5 sensor, because they can block the capillary. Another issue are reactions at the cell surface that may cause contamination of the cell or formation of water and thus can result in erroneous readings.

A number of two moisture analysis points is usually the recommended minimum (one immediately after dehydration and another further downstream). If a fault develops at one location, then the second location will act as a backup.

3.6 Development of process selection guidance

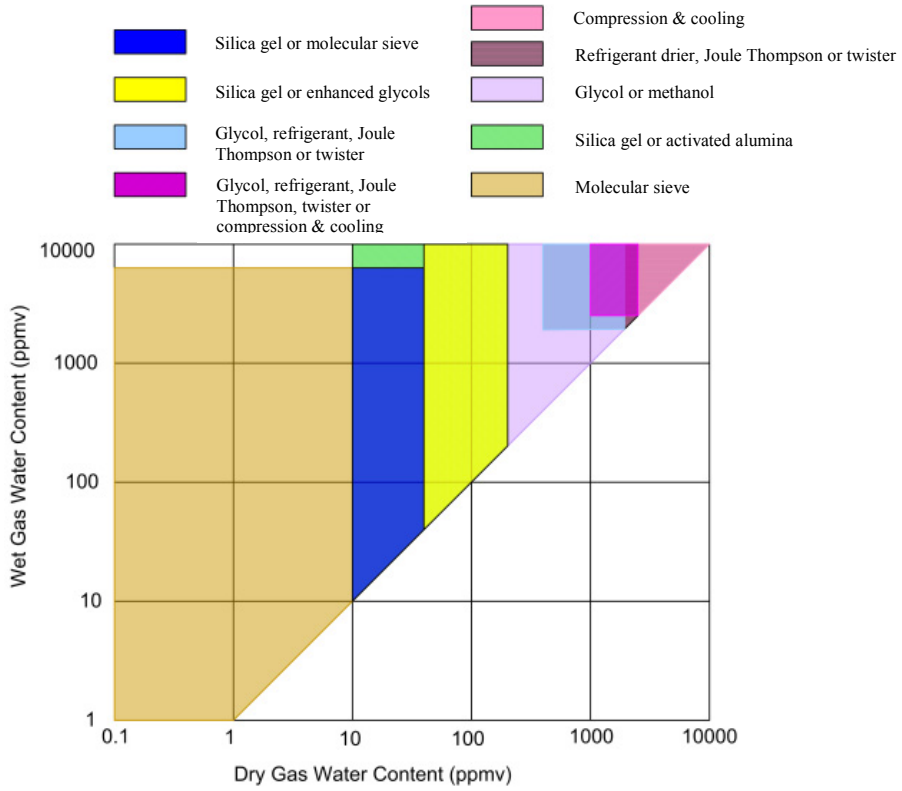

Fig. 7. Ranges of applicability of different dehydration technologies.

Fig 7 illustrates the zones of dehydration in relation to technology options. In some ranges there are multiple technology options with selection driven by factors other than simply water content. For low water content requirements multiple technology options can be used, typically bulk removal during compression and molecular sieves post compression.

Under most circumstances, it is invariably cheaper to offload the final dehydration system by use of more basic techniques, if their application is feasible. In case of water-saturated, low-pressure gas it is beneficial to use the compression/cooling equipment (which is mandatory to reach the export conditions) to raise the pressure, knockout the condensed water and reduce the gas equilibrium moisture content as part of the normal compression process. This has the following effects:

- Minimization of the moisture that enters the final dehydration package.
- Reduction of the actual volume of raw gas in the final dehydration plant, which results in smaller equipment.

The presence of certain impurities can physically damage molecular sieve desiccants. Installation of a short section of guard bed (containing silica gel or activated alumina) immediately above the molecular sieve bed can help avoiding deterioration. However, the guard bed will have a design life and once aging starts it will no longer offer protection to the molecular sieve. Sacrificial guard beds might need treatment as hazardous waste, while regenerable guard beds would require additional energy.

Using multiple dehydration techniques in series is possible. For example, compression/cooling, followed by a TEG system, followed by molecular sieve polishing unit. The benefits of such systems depend on the individual process requirements. They can provide a higher level of product moisture integrity in the event of a malfunction. The extent of capital cost penalty will be process specific.

In the event that a second molecular sieve dehydration train is necessary to process the gas, installing a TEG system upstream can offload the regular molecular sieve system. Smaller adsorber bed volumes and/or increased bed adsorption time will result. For each specific application, a cost-benefit analysis is essential to determine the most cost effective option.

3.7 Further research requirements

Several areas need additional work to enable a full and adequate consideration of dehydration processes and issues. This work identified the following key areas for further investigation:

- The effects of inerts and impurities on physical properties of CO_2, as both can cause significant changes in the phase envelop and saturated water content of CO_2.
- Modification of the related physical properties estimation methods, i.e. equations of state, and models.
- Clarification and quantification of the hydrate formation issue for CCS applications.
- Re-engagement of vendors. Their opinions on CCS as a market seem to have changed, potentially because of the cancellation of certain major CCS projects and the DECC and NER300 competitions.
- Research on membranes for dehydration of supercritical CO_2.
- Development and improvement of acid-resistant solid desiccants that can better deal with impurities. Vendors are currently working on this sensitive area of research, but are not willing to discuss it yet.

IEAGHG has recently commissioned a study on the detailed impact of CO_2 impurities on compression, liquefaction and transport to Newcastle University and University of Edinburgh [27].

4. Conclusions

The purpose of this work was to examine the characteristics of the various dehydration processes and their integration into CCS systems.

A number of suitable technologies for CO_2 dehydration already exist, with molecular sieve and TEG systems as the most likely technologies for implementation. Due to limitations in the data disclosed by the vendors, the cost and operating information presented in this paper is preliminary, fragmentary and associated with some uncertainties. However, for new CCS installations, these uncertainties will only have a little effect, since the dehydration unit is a small part of a large, high-capital project.

Design and operation of dehydration units come along with several challenges. This work identified that it is usually beneficial in terms of economics to consider a series of dehydration techniques in order to offload the main system. Besides, removal of impurities by application of guard beds and upstream treatment can offer protection for sensitive desiccants.

The minimum CAPEX and OPEX for both molecular sieve and TEG systems depend mainly on operating pressure and type of regeneration. For a fixed operating pressure, there is a wide spread in CAPEX data. In case of high inerts, the CAPEX will increase for both molecular sieve and TEG systems. Presence of impurities, i.e. NO_x, SO_x and H_2S, leads to a 7% higher CAPEX but no difference in OPEX for molecular sieve systems. At this time, it is not possible to quantify the effect of impurities on the costs of TEG systems.

Areas requiring further work are, for example, the effect of inerts and impurities on the physical properties of the CO_2 stream. Some vendors indicated that interest in CCS projects might be limited in the near future, so it seems that re-engagement of the vendors will be important for future projects and studies.

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